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SURFACE ACTIVITY AND STABILIZING ABILITY OF NEW BIOLOGICAL SURFACTANTS

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Abstract

Biosurfactants are surface-active molecules produced by microorganisms and offer several advantages including low toxicity, high biodegradability, remain active at extreme pH and salinity. These potential advantages make them useful in several applications such as ecofriendly construction mixtures, health care products, cosmetics, food and oil industries. Currently, industrial and residential construction is developing rapidly, and this requires the manufacture of concrete structures of increased strength, high reliability and durability. In this regard, a very urgent problem is the creation of cement-concrete compositions with good rheological and structure-forming properties. To effectively solve these problems, it is necessary to widely use special plasticizing surfactant additives for cement mixtures. The purpose of this work is to investigate colloidal chemical properties of new biological surface-active substances depending on the concentration and temperature, and their effectiveness for disperse systems equilibration. Different methods for the measurements of properties and efficiency of new biosurfactants were used. The effects of concentration and temperature on the surface-activity and foaming abilities of new biological surface-active substances were studied. It has been established that with an increase in the concentration of biosurfactants and the temperature of the system, the surface activity and stabilizing ability of new biosurfactants were increased. The effect of new biosurfactants on the technological properties of cement slurries was studied. It has been shown that, at low concentrations, the retarding effect of new biosurfactants increases linearly with an increase in their concentration and surface activity. In this case, the formation of biosurfactant adsorption layers leads to a decrease in the hydration of cement particles. It has been established that at high concentrations adsorption of biosurfactant aggregates on the cement surface occurs, which leads to increased stability of the dispersion and a sharp decrease in the setting rate of the cement mass. By choosing the concentration of biosurfactant additives, it was possible to control the setting time and strength of cement stone, which can be used in the production of cement-concrete compositions and building materials.

Keywords: surfactants, surface activity, foam-forming ability, adsorption, disperse systems, plasticizing effect.

INTRODUCTION

Biosurfactants are surface-active molecules produced by microorganisms, either on the cell surface or secreted extracellularly. They form a thin film on the surface of microorganisms and help in their detachment or attachment to other cell surfaces. Microbial surfactants offer several advantages over synthetic ones, such as low toxicity, high biodegradability, remain active at extreme pH and salinity. Biosurfactants are produced by bacteria, yeasts, and filamentous fungi [1-3]. The composition and yield of biosurfactants depends on bioreactor characteristics, pH of the medium, nutrient composition, agitation, oxygen availability and temperature of the system. Depending on the nutrients, agitation, pH and temperature of the medium it is possible to obtain biosurfactants with different chemical structure. Depending on the chemical structure of the biosurfactants they have several categories such as glycolipids, lipopeptides, lipoproteins, polymeric and particulate surfactants [4-5]. Biosurfactants are composed of a hydrophilic moiety made up of amino acids, peptides, polysaccharides and a hydrophobic moiety consisting of fatty acids. Biosurfactants can be used to replace chemical surfactants, as they are environment-friendly, less toxic, biodegradable in nature, have higher foaming ability, and possess lower CMC values than the chemical surfactants. These potential advantages make them useful in several applications like ecofriendly construction mixtures with cement, bioremediation, health care products, cosmetics, food and oil industries. Well known that currently, industrial and residential construction is developing rapidly, and this requires the manufacture of concrete structures of increased strength, high reliability and durability. In this regard, a very urgent problem is the creation of cement-concrete compositions with good rheological and structure-forming properties. To effectively solve these problems, it is necessary to widely use special plasticizing additives for cement mixtures [6-7]. Surfactants are often used as plasticizing additives, which increase mobility, reduce stiffness and dilute the concrete mixture, which reduces energy and labor costs when laying concrete in monolithic building structures and precast concrete products and contributes to the intensification of the technological cycle and increase product quality [8-9]. The effect of surfactants on the properties of surfaces and their use in regulating the characteristics of disperse systems is due to their ability to lower the surface energy by being adsorbed at the interfaces [9-10]. Due to this, surfactants are widely used to control various technological processes and improve the quality of a wide variety of materials, characterized by the presence of a highly developed interface [11-12]. Many processes cannot proceed without the participation of surfactants, for example, the stabilization of foams, modification of various surfaces, regulation of cement slurries to produce high-quality materials [12]. The multifaceted action of surfactants is based on the processes of their adsorption on the surface of solid particles. The introduction of surfactants into cement slurries is gaining increasing importance in order to give them the necessary structural and mechanical properties, and regulate the technological characteristics [12-13]. The growth of the production of new biosurfactants makes it possible widely use them to regulate the properties of disperse systems [14]. However, it is necessary to select and test new surfactants and find effective regulators of cement disperse systems. Some studies of the properties of cement slurries with surfactants showed the possibility of changing the general course of the setting process and subsequent hardening of the cement mortar [15-16]. Surfactant molecules are adsorbed on the hydrophilic surface of cement particles and formed an adsorption layer of oriented surfactant molecules [17-18]. At present, the volumes of production of surfactants do not meet the necessary requirements of the construction industry. It should also be noted that there are still unresolved issues of optimizing the range of surfactants for the creation of strong and reliable construction and concrete products [19-20]. Therefore, it is very important to study and find out new polyfunctional biosurfactants with high plasticizing properties of cement slurries. In this regard, it is very interesting to identify the effectiveness of the new biosurfactants and their compositions on cement-concrete mixtures, the creation of modified mineral additives with polyfunctional surfactants, to make new cement compositions and concrete mixtures with improved rheological properties and high strength for industrial and residential constructions [21-22]. The purpose of this work is to investigate surface activity and colloidal chemical properties of new biological surface-active substances depending on the concentration and temperature, and their effectiveness for disperse systems equilibration. The article presents the materials and methods used in the work, the results of the study and their discussion, conclusion based on the analysis of the results and a list of references.

METHODS AND MATERIALS

The purpose of this work was obtaining of new biological surface-active substances from Saccharomyces cerevisiae depending on temperature of the system and establishing correlations between their surface activity and colloid-chemical properties, stabilizing ability of new biosurfactants in disperse systems. To achieve the goal, the following tasks were set: obtaining of new biological surface-active substances from biomass by separation methods and purification by extraction, distillation and recrystallization methods; study surface activity and stabilizing abilities of new biosurfactants. Following methods were used:

Extraction and purification of biological surfactants. Biological surfactants were isolated by acid precipitation and purified by solvent extraction. The Saccharomyces cerevisiae were cultivated in medium with nutrients mannite, glucose, dextrose, saccharine, glycerol and stored in a thermostat at a constant temperature. Each experiment was conducted at different temperatures in a thermostat. After incubation at a constant temperature for 120 hours in a thermostat, the cells were removed from the cultural liquid by centrifugation for 20 minutes at a constant temperature. The cell-free supernatant thus obtained was acidified with a 10% aqueous solution of acetic acid and the resulting mixture was stored for 18 hours at a constant temperature in an incubator to enhance the precipitation of biological surfactants. The precipitate formed as a result of storage in a thermostat was separated by centrifugation for 20 minutes. The thus isolated precipitate was extracted several times with chloroform-methyl alcohol 1:2 mixture (Folch solution) at room temperature. The resulting extract was filtered and then the solvent in the extract was distilled under reduced pressure. The residue in the flask after distillation was dissolved in ethanol-acetone and reprecipitated with n-hexane. The biological surfactants isolated after reprecipitation were dried in a thermostat under reduced pressure. Biological surfactants obtained in this way were reddish-brown, viscous substances with a peculiar odor. Depending on the nutrients and temperature of the medium with nutrients during the experiments obtained biosurfactants have names BS-1, BS-2, and BS-3.

Determination of surface tension. The surface tension of surfactant solutions was determined using tensiometer DCAT-9T at different temperatures and concentrations. In order to obtain statistically significant results, each measurement was repeated 5 times.

Foaming ability. The foaming ability was determined at a temperature of 293K, while 100 ml of a freshly prepared surfactant solution with a certain concentration was shaken in a graduated container for 60 s. Then the height of the foam column at the initial moment in the graduated container was measured.

Thin layer chromatography. Thin layer chromatography (TLC) was carried out at room temperature in two systems: a. acetone, toluene, ethanol 3:1:1. b. acetone, benzene, ethanol 2:1:2. For the study, ascending TLC was used in chambers preliminarily saturated with solvent vapors forming the mobile phase. Chromatography was carried out on plates with a polar stationary phase on aluminum and polymer matrices.

Refractive indices of aqueous solutions of surfactants. An Easy plus refractometer was used to determine the refractive index (n_D^{20}) of aqueous solutions of the obtained new surfactants. The refractive index of aqueous solutions was measured at a temperature of 293 K.

Density of surfactant samples. To determine the density (d_4^{20}) of new surfactants a density meter Easy plus was used. The density of the obtained surfactants was measured at a temperature of 293 K.

Investigation of the spreadability of cement slurry. To study the spreadability of the cement mortar, the circle of the spread of the test mortar on flat glass was determined after pouring it out of a bottomless cone. The method fixes the diameter of a circle that blurred at some point in time with a strictly defined composition (water/solid constituent/chemical reagents).

Determination of the setting time of cement paste. To determine the setting time of the cement paste, a Vicat device with a needle was used. The time elapsed from the beginning of mixing (the moment of pouring water) to the moment when the needle does not reach the plate by 2-4 mm was considered the beginning of the setting of the cement paste. The end of the setting of the cement paste was considered the time from the beginning of mixing to the moment when the needle is lowered into the dough by no more than 1–2 mm.

Determination of the density of the cement mixture. The density of the cement mixture was characterized by the ratio of the mass of the compacted mixture to its volume and was expressed in g/cm^3. A steel cylindrical vessel with a capacity of 1000 ml was used for testing.

The vacuum distillation and recrystallization methods were used to purify the surfactants.

RESULTS AND THEIR DISCUSSION

Biosurfactants are environment-friendly, less toxic, biodegradable in nature, have higher foaming ability, and possess lower critical micelle-forming concentration values than the synthetic surfactants and so can be used to replace synthetic surfactants. Among the numerous surface-active substances that are widely used in practice, biological surfactants are poorly studied. In this regard, the work carried out a study of the surface activity, the colloidal-chemical properties, the effect of concentration and temperature on the surface-active and adsorption capacity of new biosurfactants. The new biological surfactants were isolated by acid precipitation and purified by solvent extraction. The physic-chemical properties of new biological surface-active substances are presented in table 1 below.

Table 1. The physic-chemical properties of new biologic surface-active substances.

Abbreviation of surfactant	Appearance of surfactant	Optic density, D	R_f	n_D^{20}	d_4^{20}	Electro-conductivity
BS-1	Reddish-brown, viscous substance	1,2565	0,75; 0,83	1,4833	1,14	4,858
BS-2	Dark- brown, viscous substance	1,2874	0,64; 0,72	1,5142	1,18	4,236
BS-3	Brown, viscous substance	1,2367	0,62; 0,71	1,5385	1,22	4,564

*Rf – Thin layer chromatogram retention factor.

The isolated and purified biological surfactants were weighed and aqueous solutions with different concentrations were prepared from them. The surface activity, disperse systems stabilizing ability of new biological surfactants in water solutions were investigated. The results of a study of the surface tension of aqueous solutions of the studied new biologic surface-active substances are shown in Table 2 below. Analysis of the obtained experimental data in Table 2 showed that the studied surfactants are located in the following order in terms of surface activity: BS-3 > BS-2 > BS-3. It can be seen that with an increase in the biosurfactant concentration and temperature of the system, the surface activities of new biosurfactants were increased.

Table 2. The surface tension of aqueous solutions of the studied biosurfactants depending on the concentration and temperature.

Surfactant	T, K	Surface tension (mN/m) at different surfactant concentrations in the solution ($C \cdot 10^2$ mol/l)								
		5	2,5	1,25	0,62	0,31	0,16	0,08	0,04	0,02
BS-1	293	32,0	33,3	37,7	44,2	51,3	62,3	66,5	68,6	70,4
	303	31,4	33,4	37,4	43,4	50,4	60,4	65,3	67,5	69,6
	313	30,1	32,3	36,2	42,3	49,3	56,5	64,5	66,3	69,0
	323	29,1	31,4	35,3	41,4	48,3	55,3	61,4	65,2	68,1
	333	28,2	31,2	33,4	40,2	47,4	53,4	59,5	63,4	66,6
BS-2	293	32,0	35,2	38,0	44,2	51,3	61,2	66,1	70,1	70,5
	303	31,1	33,1	37,1	43,0	50,1	60,0	65,1	69,0	70,1
	313	30,0	32,0	35,1	42,1	49,1	56,1	64,2	67,2	69,4
	323	29,0	32,0	34,0	41,2	48,0	55,0	60,1	65,3	68,3
	333	28,1	31,2	35,3	40,1	47,3	51,2	59,3	64,2	67,1
BS-3	293	29,1	30,4	33,5	40,5	52,5	56,3	62,5	66,3	68,3
	303	28,2	29,1	31,3	40,3	47,8	55,0	61,1	64,2	67,2
	313	27,3	27,0	31,4	38,7	44,4	53,3	58,6	63,4	66,3
	323	26,0	26,9	29,1	37,3	43,1	51,6	57,1	61,4	66,1
	333	25,4	25,1	28,4	36,8	42,4	49,5	56,0	59,5	60,5

The stabilizing abilities of new biological surface-active substances were investigated. As well as the effect of system temperature and surfactant concentration on the foaming ability of new biosurfactants were studied. The results of studies of the foaming ability of new biosurfactants depending on their concentration in aqueous solutions at different temperatures of the system are shown in Table 3 below. As can be seen from the experimental research results (Table 3), with an increase in the concentration of biosurfactants in the solution and temperature of the system the foam-forming abilities of biosurfactants were increased. It should also be noted that there is a good correlation between the foaming ability and the surface activity of the studied biologic surface - active substances.

Table 3. Foam-forming abilities of new biosurfactants depending on their concentration in aqueous solutions and temperature of the system.

Surfactant	T, K	Foam-forming ability (V, ml) at different surfactant concentrations (g/l)					
		0,1	0,5	0,62	1,25	2,5	5,0
BS-1	293	174	212	221	267	283	332
	313	190	234	245	288	321	350
	333	202	245	261	305	331	352
BS-2	293	181	220	227	272	291	341
	313	195	240	253	295	330	357
	333	207	252	267	311	341	361
BS-3	293	185	222	231	277	294	344
	313	200	244	257	300	335	361
	333	211	256	271	316	345	364

As can be seen from Table 3, the surfactant BS-3 has the highest foam forming ability and with increasing temperature of the system, the foam forming ability was increased sharply, which was associated with a change in the kinetic parameters of the adsorption of biosurfactant molecules at the interfacial interface.

The effect of new biosurfactants on the technological properties of cement slurries was studied. Technological characteristics of cement slurries with biosurfactant additives are presented in Table 4 below. The obtained results showed that new biological surface-active substances were effective retarders of the setting time of cement slurries. At optimal concentrations of such biosurfactants, the setting time of cement slurries increases up to 4.5-5.0 hours. The analysis of the obtained results showed that the presence of an ester bonds, hydroxyl and carboxyl groups in the structure of the molecules of the studied biosurfactants enhance their effectiveness in slowing down the setting of cement suspensions. It was found that the presence of hydroxyl groups in the structure of surfactant molecules was effective for slowing down the setting of cement slurries. It was also interesting to note the effect of the concentration of the biosurfactants on the setting time of cement slurries. Studies have established that with an increase in the concentration of the biosurfactants, the effectiveness of slowing down the setting of cement slurries was increased. The results obtained the research work (Table 4) showed, that at low concentrations, the retarding effect of biosurfactants was increased linearly with an increase in their concentration and surface activity. At low biosurfactant concentrations, the formation of adsorption monolayers was observed, which leads to a decrease in the hydration of cement particles. However, at higher biosurfactant concentrations (above CMC), the effectiveness of slowing down the setting of cement slurries was increased significantly.

Table 4. Technological characteristics of cement slurries with the addition of new biosurfactants at 80°C and water/cement ration 1:1.

No.	Surfactant	Surfactant quantity	Spreadability, см	Density, кг/м^3	Setting time, h.-min.	
					Start	End
1.	BS-1	0,0	22,0	1790	0-50	1-40
		0,1	19,5	1790	0-55	1-50
		0,3	18,5	1790	1-10	2-15
		1,0	27,0	1795	2-15	3-15
		2,0	27,5	1800	3-25	4-35
2.	BS-2	0,0	22,0	1790	0-50	1-50
		0,1	22,5	1790	0-65	1-55
		0,3	23,5	1795	1-55	2-25
		1,0	19,0	1800	2-45	3-35
		2,0	20,0	1805	3-55	4-50
3.	BS-3	0,0	22,0	1790	0-50	1-55
		0,1	25,5	1795	2-10	2-50
		0,3	26,0	1800	2-25	3-25
		1,0	26,5	1800	3-35	4-50
		2,0	27,5	1850	4-15	5-00

The obtained results were associated with the adsorption of micellar particles on the surface of the cement, which leaded to an increased aggregative stability of the cement dispersion, and, accordingly, a decrease in the setting rate of the cement mass.

CONCLUSION

The colloid-chemical properties of new biological surface-active substances (BS-1, BS-2, BS-3) have been investigated. The effects of concentration and temperature on the surface-active and foaming abilities of new biosurfactants were studied. It has been established that with an increase in the concentration of biosurfactants and the temperature of the system, the surface activity and foam forming ability of new biosurfactants were increased. It has been shown that new biosurfactants were effective retarders of the setting time of cement dispersed systems. It has been established that with an increase in the concentration of biosurfactants, the effectiveness of slowing down the setting of cement slurries was increased. It has been shown that, at low biosurfactant concentrations, the retarding effect of biosurfactants was increased linearly with an increase in their concentration and surface activity. In this case, the formation of biosurfactant adsorption layers leads to a decrease in the hydration of cement particles. It was established that at biosurfactant concentrations above CMC, the effectiveness of setting delay increases significantly, due to the adsorption of biosurfactant micellar particles on the cement surface. By choosing the concentration of biosurfactant additives, it was possible to control the setting time and strength of cement stone, which can be used in the production of cement-concrete compositions and building materials.

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CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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